Quantum statistics

Density operator:

$$\rho \equiv \sum_i w_i |\alpha_i\rangle\langle\alpha_i|$$

is

- Hermitean:
$$\rho^\dagger = \rho$$
- normalized:
$$\mathrm{tr}\rho = 1.$$

Density matrix:

$$\langle b''|\rho|b'\rangle = \sum_i w_i \langle b''|\alpha_i\rangle\langle\alpha_i|b'\rangle.$$

Ensemble average:

$$\begin{aligned}[A] &= \sum_{b'}\sum_{b''}\langle b''|\rho|b'\rangle\langle b'|A|b''\rangle \\ &= \mathrm{tr}(\rho A).\end{aligned}$$

Dynamics

$$|\alpha_i\rangle = |\alpha_i; t_0\rangle \longrightarrow |\alpha_i, t_0; t\rangle$$

We suppose that the occupation of states is conserved, i.e.

$$w_i = \text{constant}.$$

Now

$$\rho(t) = \sum_i w_i |\alpha_i, t_0; t\rangle\langle\alpha_i, t_0; t|,$$

so

$$\begin{aligned} i\hbar\frac{\partial\rho}{\partial t} &= \sum_i w_i \left(i\hbar\frac{\partial}{\partial t}|\alpha_i, t_0; t\rangle\right)\langle\alpha_i, t_0; t| \\ &\quad + \sum_i w_i |\alpha_i, t_0; t\rangle\left(-i\hbar\frac{\partial}{\partial t}|\alpha_i, t_0; t\rangle\right)^\dagger \\ &= H\rho - \rho H = -[\rho, H].\end{aligned}$$

Like Heisenberg's equation of motion, but wrong sign! OK, since ρ is not an observable.

Continuum

Example:

$$[A] = \int d^3x' \int d^3x'' \, \langle \boldsymbol{x}''|\rho|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|A|\boldsymbol{x}''\rangle.$$

Here the density matrix is

$$\begin{aligned}\langle\boldsymbol{x}''|\rho|\boldsymbol{x}'\rangle &= \langle\boldsymbol{x}''|\left(\sum_i w_i|\alpha_i\rangle\langle\alpha_i|\right)|\boldsymbol{x}'\rangle \\ &= \sum_i w_i \psi_i(\boldsymbol{x}'')\psi_i^*(\boldsymbol{x}').\end{aligned}$$

Note

$$\langle\boldsymbol{x}'|\rho|\boldsymbol{x}'\rangle = \sum_i w_i|\psi_i(\boldsymbol{x}')|^2.$$

Thermodynamics

We define

$$\sigma = -\mathrm{tr}(\rho\ln\rho).$$

One can show that

- for a completely stochastic ensemble
$$\sigma = \ln N,$$
when N is the number of the independent states in the system.
- for a pure ensemble
$$\sigma = 0.$$

Hence σ measures disorder $\Longrightarrow$ it has something to do with the entropy.
The entropy is defined by

$$S = k\sigma.$$

In a thermodynamical equilibrium

$$\frac{\partial\rho}{\partial t} = 0,$$

so

$$[\rho, H] = 0$$

and the operators ρ and H have common eigenstates $|k\rangle$:

$$\begin{aligned} H|k\rangle &= E_k|k\rangle \\ \rho|k\rangle &= w_k|k\rangle.\end{aligned}$$

Using these eigenstates the density matrix can be represented as

$$\rho = \sum_k w_k|k\rangle\langle k|$$

and

$$\sigma = -\sum_k \rho_{kk}\ln\rho_{kk},$$

where the diagonal elements of the density matrix are

$$\rho_{kk} = w_k.$$

In the equilibrium the entropy is at maximum.
We maximize σ under conditions

- $U = [H] = \mathrm{tr}\rho H = \sum_k \rho_{kk}E_k$.
- $\mathrm{tr}\rho = 1$.

Hence

$$\begin{aligned}\delta\sigma &= -\sum_k \delta\rho_{kk}(\ln\rho_{kk} + 1) = 0 \\ \delta[H] &= \sum_k \delta\rho_{kk}E_k = 0 \\ \delta(\mathrm{tr}\rho) &= \sum_k \delta\rho_{kk} = 0.\end{aligned}$$

With the help of Lagrange multipliers we get

$$\sum_k \delta\rho_{kk}\left[(\ln\rho_{kk}+1)+\beta E_k+\gamma\right]=0,$$

so

$$\rho_{kk}=e^{-\beta E_k-\gamma-1}.$$

The normalization ($\mathrm{tr}\rho=1$) gives

$$\rho_{kk}=\frac{e^{-\beta E_k}}{\sum_l^N e^{-\beta E_l}}\quad\text{(canonical ensemble).}$$

It turns out that

$$\beta=\frac{1}{k_BT},$$

where T is the thermodynamical temperature and k_B the Boltzmann constant.

In statistical mechanics we define *the canonical partition function* Z:

$$Z=\mathrm{tr}e^{-\beta H}=\sum_k^N e^{-\beta E_k}.$$

Now

$$\rho=\frac{e^{-\beta H}}{Z}.$$

The ensemble average can be written as

$$\begin{aligned}[A] &= \mathrm{tr}\rho A=\frac{\mathrm{tr}\left(e^{-\beta H}A\right)}{Z}\\ &= \frac{\left[\sum_k^N\langle k|A|k\rangle e^{-\beta E_k}\right]}{\sum_k^N e^{-\beta E_k}}.\end{aligned}$$

In particular we have

$$\begin{aligned}U &= [H]=\frac{\sum_k^N E_k e^{-\beta E_k}}{\sum_k^N e^{-\beta E_k}}\\ &= -\frac{\partial}{\partial\beta}(\ln Z).\end{aligned}$$

Example Electrons in a magnetic field parallel to z axis. In the basis $\{|S_z;\uparrow\rangle,|S_z;\downarrow\rangle\}$ of the eigenstates of the Hamiltonian

$$H=\omega_c S_z$$

we have

$$\rho\mapsto\frac{\begin{pmatrix}e^{-\beta\hbar\omega_c/2} & 0\\ 0 & e^{\beta\hbar\omega_c/2}\end{pmatrix}}{Z},$$

where

$$Z=e^{-\beta\hbar\omega_c/2}+e^{\beta\hbar\omega_c/2}.$$

For example the ensemble averages are

$$\begin{aligned}[S_x] &= [S_y]=0,\\ [S_z] &= -\left(\frac{\hbar}{2}\right)\tanh\left(\frac{\beta\hbar\omega_c}{2}\right).\end{aligned}$$